

PATENT SPECIFICATION

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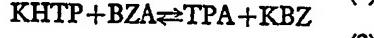


(54) PRODUCTION AND RECOVERY OF TEREPHTHALIC ACID

(71) We, PHILLIPS PETROLEUM COMPANY, a corporation organised and existing under the laws of the State of Delaware, United States of America, of 5 Bartlesville, Oklahoma, United States of America, do hereby declare the invention for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in 10 and by the following statement:—

This invention relates to the production of terephthalic acid by the reaction of dipotassium terephthalate with benzoic acid and to the purification of terephthalic acid so obtained.

It is known in the art that dipotassium terephthalate can be produced by the disproportionation of potassium benzoate using zinc benzoate to catalyze the reaction. See, 20 for example, U.S. Patent 2,838,230. It is also known that terephthalic acid can be produced by the reaction of dipotassium terephthalate with benzoic acid. See, for example, U.S. Patent 2,930,813. When dipotassium terephthalate is reacted with benzoic acid to produce terephthalic acid, the reaction proceeds in two steps as follows:



30 wherein K_2TP is dipotassium terephthalate, BZA is benzoic acid, KHTP is potassium hydrogen terephthalate (also called potassium acid terephthalate), KBZ is potassium benzoate and TPA is terephthalic acid. As indicated 35 by equation (1) and (2), this reaction proceeds in two steps. While step (1) proceeds nearly to completion, step (2) is reversible and, accordingly, the potassium acid terephthalate is only about 80 percent converted to terephthalic acid under equilibrium conditions.

Terephthalic acid is of considerable im-
 [Price 33p]

portance in industry as a starting material in such applications as the manufacture of synthetic fibres of the polyester type; therefore, there has been considerable activity in the art directed toward the economic and convenient production of large quantities of relatively pure terephthalic acid. One problem encountered in relation to the preparation of terephthalic acid in accordance with equation (1) and (2) above has been in obtaining complete reaction of the potassium acid terephthalate in order to maximize the production of terephthalic acid from the dipotassium terephthalate starting material and in the separation of the terephthalic acid product from the crude reaction mixture.

In accordance with this invention there is provided a process for the preparation and recovery of terephthalic acid from an aqueous solution of dipotassium terephthalate, which comprises, in sequence,

- (i) reacting the dipotassium terephthalate in said solution with benzoic acid to produce an aqueous slurry containing dissolved potassium benzoate and undissolved benzoic acid, potassium hydrogen terephthalate, and terephthalic acid;
- (ii) countercurrently contacting said slurry in an elongated contacting zone with a stream of water, the temperature in said zone adjacent the upstream end (considered in the direction of travel of the slurry) being maintained at a temperature in the range 38—66°C. and adjacent the downstream end at a lower temperature, such lower temperature being in the range 10—38°C.;
- (iii) recovering from said upstream end an aqueous solution of potassium benzoate and from said downstream end an aqueous slurry of benzoic acid, potassium hydrogen terephthalate and terephthalic acid;
- (iv) countercurrently contacting the slurry

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recovered in step (iii) in a second elongated contacting zone with a second stream of water, the temperature in said second zone adjacent the upstream end (considered in the direction of travel of the slurry) being maintained at a temperature in the range 66—121°C. and adjacent the downstream end at a lower temperature, such lower temperature being in the range 24 to 66°C.;

(v) recovering from the upstream end of said second zone a second aqueous solution of potassium benzoate and from the downstream end an aqueous slurry of terephthalic acid; and

(iv) separating the terephthalic acid from the slurry recovered in step (v).

By this process there is produced a terephthalic acid product of high purity and, in addition, the reaction in equation (2) above proceeds to substantial completion thus making unnecessary the removal of unreacted potassium acid terephthalate.

The invention will be further described with reference to the accompanying drawings.

Referring to the drawing, which is a schematic diagram showing a preferred process according to this invention, there is introduced into stirred reactor 1, equipped with stirring means 2, benzoic acid via line 3 and dipotassium terephthalate dissolved in water via line 4. In stirred reactor 1 the benzoic acid and dipotassium terephthalate solution are heated to a temperature in the range 66—149°C, preferably about 88°C, with stirring for a time period of about 15 minutes during which time the benzoic acid and dipotassium terephthalate react and reach equilibrium. In reactor 1 a two-step reaction occurs in which (1) dipotassium terephthalate reacts with benzoic acid to yield potassium acid terephthalate and potassium benzoate and thereafter (2) the potassium acid terephthalate reacts with benzoic acid to yield terephthalic acid and potassium benzoate. Upon reaching equilibrium in reactor 1, essentially all the dipotassium terephthalate is converted to potassium acid terephthalate but only about 75 to 80 percent of the potassium acid terephthalate reacts with benzoic acid to produce terephthalic acid. Accordingly, at equilibrium there is a reaction mixture in reactor 1 comprised essentially of potassium benzoate benzoic acid, potassium acid terephthalate and terephthalic acid. This reaction mixture is in the form of an aqueous slurry having dissolved material and undissolved material wherein the solids portion of the slurry that is the undissolved material, is comprised of benzoic acid, potassium acid terephthalate, and terephthalic acid. The dissolved portion of the slurry is comprised

essentially of potassium benzoate, a minor portion of benzoic acid also being present in solution.

The slurried reaction mixture from reactor 1 is introduced into wash column 5 via line 6. Prior to the introduction of the reaction mixture into column 5, it is diluted with water to produce a slurry containing in the range of about 5 to 50 weight percent solids, preferably 15 weight percent solids. The water diluent is introduced into line 6 via line 7. In addition, the diluted reaction mixture is cooled from the reactor temperature to a temperature in the range 38°—66°C, preferably 49°C. This cooling can be effected by any means such as by introducing chilled water into line 6 via line 7 to thus both cool and dilute the reaction mixture.

In settled bed wash column 5, the reaction mixture from reactor 1, which is introduced into the upper portion of column 5, undergoes phase separation wherein the undissolved material containing the above-mentioned solid constituents settles to the lower portion of column 5 and the potassium benzoate-containing dissolved material accumulates in the upper portion.

Potassium acid terephthalate is relatively insoluble in a relatively concentrated aqueous solution of potassium benzoate at temperatures maintained in the upper portion of column 5; however, potassium acid terephthalate is appreciably soluble in relatively dilute aqueous solutions of potassium benzoate at those temperatures. Since the concentration of potassium benzoate in solution decreases from the upper portion of column 5 to the lower portion of column 5, it becomes necessary to operate the lower portion of column 5 at a temperature less than the upper portion of column 5 to prevent dissolution of potassium acid terephthalate into water containing a relatively low concentration of potassium benzoate. Therefore, to promote the solubility of potassium benzoate and to maintain the remaining constituents of the reaction mixture in the solid state, column 5 is operated under a temperature gradient with the upper portion of column 5 being maintained at the indicated temperature higher than the lower portion of column 5. This temperature gradient is for the purpose of facilitating the removal of potassium benzoate, in solution, from the upper portion of column 5 via line 8, and for the removal of the remaining solid constituents of the reaction mixture from the lower portion of column 5 via line 9.

In this preferred embodiment it has been found that column 5 operates most efficiently with the upper portion maintained at a temperature of about 49°C and the lower portion at a temperature of about 27°C. With the upper portion of column 5 at this tem-

perature there is effected maximum removal of potassium benzoate.

5 The temperatures of the upper and lower portions of column 5 may be maintained at the desired levels by any means known in the art such as by heat exchange jackets 10 and 14 through which are passed suitable heat exchange media via lines 11 and 12 and 15 and 16 respectively.

10 Conveniently the water introduced into the lower portion of column 5 via line 13 is at a temperature of approximately 27°C.

15 The material in the lower portion of column 5, which is a slurry comprised essentially of benzoic acid, potassium acid terephthalate and terephthalic acid in undissolved state, is passed via line 9, pump 17 and heating means 18 and introduced into the upper portion of a second column 19.

20 In order to complete the conversion of the original dipotassium terephthalate to terephthalic acid it is necessary to place the potassium acid terephthalate and benzoic acid, both of which are in solid state in the lower

25 portion of column 5, in solution so that they can react to form terephthalic acid and potassium benzoate. This solution is conveniently effected by heating the slurry in heating means 18 to a temperature in the range 66°—

30 121°C. preferably about 88°C. and then introducing the stream in line 9 into column 19 at this temperature.

In column 19, the potassium acid terephthalate and benzoic acid contained in the slurry recovered from reactor 1 react to form potassium benzoate and additional terephthalic acid. The terephthalic acid settles to the lower portion of column 19 and the potassium benzoate thus formed, being

35 soluble, remains in the upper portion of column 19. Water, at a temperature of approximately 38°C. is introduced into the lower portion of column 19 via line 20 and rises through column 19 in countercurrent

40 contact with the settling material, which is comprised essentially of terephthalic acid, to remove, from the solid terephthalic acid, impurities such as unreacted potassium acid terephthalate, benzoic acid and potassium benzoate. These impurities are then removed

45 from the upper portion of column 19 via line 21 for further processing, not shown.

Column 19 is also operated under a temperature gradient, the upper portion of column 19 being maintained at a temperature higher than the lower portion. The higher temperature in the upper portion of column 19 promotes the reaction of the benzoic acid and the potassium hydrogen terephthalate, whilst the lower temperature in lower portion of column 19 minimizes the solubility of terephthalic acid in the wash water introduced via line 20.

55 As already indicated the upper portion of column 19 is maintained at a temperature in

the range of 66°—121°C. preferably at about 88°C. whilst the lower portion is maintained at a temperature in the range 24°C—66°C, preferably at about 38°C.

Again, the desired temperature gradient in column 19 may be obtained by heat exchange jackets 22 and 25 through which suitable heat exchange media may be circulated via lines 23 and 24, and 26 and 27 respectively.

The contents of the lower portion of column 19 comprise a slurry of solid terephthalic acid in water and containing also minor amounts of impurities such as benzoic acid and potassium acid terephthalate. This slurry is removed from column 19 via line 28 and pump 29 and introduced into stirred wash tank 30. Water is introduced into tank 30 via line 31 and the resulting dilute slurry in tank 30 is stirred at a temperature in the range 149°—232°C. preferably about 193°C. Additional potassium benzoate is thus removed from the solid terephthalic acid by the solvent action of the hot water. The slurry is then passed from tank 30 via line 33 to filter 32 wherein the solid terephthalic acid is recovered and removed via line 34. The dissolved impurities leave in an aqueous stream via line 35. The solid terephthalic acid crystals in line 34 can be reslurried with hot water and again filtered for additional purification if desired.

It is thus seen that reactions (1) and (2) are conducted in a series of processing steps involving succeeding solid-liquid phase separation steps with water washing, each succeeding step being conducted at a successively higher temperature to thereby take advantage of the differing solubilities of the compounds and reactants involved.

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EXAMPLE

Referring again to the drawing, 640 grams of dipotassium terephthalate dissolved in 4000 grams of water was introduced into reactor 1 via line 4. Benzoic acid in the amount of 904 grams was introduced into reactor 1 via line 3. The contents of the reactor were heated to 88°C. and stirred for about 15 minutes during which time the reaction between the dipotassium terephthalate and benzoic acid reached a state of equilibrium wherein essentially all of the dipotassium terephthalate was converted to potassium acid terephthalate but only 75—80 percent of the potassium acid terephthalate was converted to terephthalic acid. The contents of reactor 1, which were in the state of a creamy slurry with the terephthalic acid and potassium acid terephthalate being present as solids, the potassium benzoate being in solution, and the benzoic acid being partly dissolved but the majority being in the solid state, were introduced into column 5 via line 6 after being first diluted with 4000 grams

of water which was introduced into line 6 via line 7 at a temperature of about 7°C. to produce a slurry containing about 16 weight percent solids at a temperature of 49°C. This slurry was introduced into the upper portion of column 5 which was 2 inches in diameter and 6 feet high wherein the solids settled to the lower portion of column 5. The upper 2 feet of column 5 was jacketed with heating jacket 10 through which heating fluid was passed to maintain the temperature of the upper portion of column 5 at 49°C. Water at 27°C. was introduced via line 13 into the bottom of column 5 and rose upward through column 5 in countercurrent contact with the settled bed of terephthalic acid-containing crystals. The water exited column 5 via line 8 carrying with it dissolved impurities, mainly potassium benzoate.

The slurry of terephthalic acid-containing material was removed from the lower portion of column 5 via line 9 and pump 17 at a rate sufficient to maintain the height of settled solid material in the lower portion of column 5 at about 20 inches above the bottom of column 5.

The upper portion of column 5 was maintained at a temperature of approximately 49°C. by passing a heating medium through heating jacket 10. In addition, the lower portion of column 5 was maintained at a temperature of approximately 27°C. by passing an appropriate heat exchange medium through heating jacket 14.

The slurry of terephthalic acid in water, which also contained unreacted potassium acid terephthalate and benzoic acid was pumped through heater 18 wherein it was

heated to 88°C. and the heated slurry was then introduced into the upper portion of column 19. The benzoic acid and potassium acid terephthalate in the slurry dissolved in the water and reacted to produce additional quantities of terephthalic acid. The terephthalic acid introduced into column 19, as well as the terephthalic acid produced in column 19, settled in the form of solid material to the lower portion of column 19, thereby forming a bed in the lower portion of column 19. Water, at a temperature of approximately 38°C., was introduced via line 20 into the lower portion of column 19, ascended through the bed of solid material and washed the material free of impurities such as unreacted potassium acid terephthalate, benzoic acid and potassium benzoate formed in the reaction of the potassium acid terephthalate and benzoic acid. These impurities were removed from column 19 via line 21.

The reaction mixture from reactor 1 was introduced into column 5 at a uniform rate over a period of 12 hours. During this same 12-hour period a total of 12,000 grams of water was introduced into column 5 via line 13 at a uniform rate. Also, a slurry from the lower portion of column 5 was introduced into the upper portion of column 19 at a constant rate over a period of about 7 hours. During this same time a total of 3750 grams of water was introduced into the lower portion of column 19 via line 20 at a constant rate.

During the course of the run samples of the effluent streams of column 5, that is, streams 8 and 9, were taken and analyzed with the results set out in Tables I and II.

Table I (Stream 8)

| Sample ⁽¹⁾ , No. | Total Solids, ⁽²⁾ grams | Solid TPA Content, grams | TPA Solids, Wt. % |
|-----------------------------|---------------------------------------|-----------------------------|----------------------|
| 1 | 6.0156 | 0.6541 | 10.9 |
| 2 | 31.7663 | 2.1356 | 6.72 |
| 3 | 63.4126 | 3.6234 | 5.71 |
| 4 | 36.2025 | 3.0607 | 8.54 |
| 5 | 38.5651 | 3.1680 | 8.21 |
| 6 | 34.4933 | 2.8940 | 8.39 |
| 7 | 35.8681 | 2.9850 | 8.32 |
| 8 | 27.0782 | 2.6894 | 9.03 |
| 9 | 37.2014 | 3.7724 | 10.14 |
| 10 | 39.1810 | 3.7553 | 9.58 |
| 11 | 40.6344 | 3.5751 | 8.80 |
| 12 | 38.9386 | 3.5649 | 9.16 |
| 13 | 7.5064 | 0.5816 | 7.75 |

(1) Each sample consisted of 900 ml except 13 which was 200 ml. The 13 samples constitute the *total* overhead washings.

(2) Consists of both dissolved (principally potassium benzoate (KBZ) and undissolved solids (principally terephthalic acid (TPA)).

The above data indicate the removal in stream 8 of a considerable quantity of potassium benzoate as tabulated under the column headed "Total Solids". From the grams listed in this column one subtracts the grams of terephthalic acid listed in the column headed "Solid TPA Content." The difference in the two amounts is the approximate total grams of potassium benzoate removed from column 5 via line 8.

Table II (Stream 9)

| | Sample ⁽¹⁾ No. | Wt. % Solids | Ash ⁽²⁾ , Wt. % |
|----|---------------------------|--------------|----------------------------|
| 10 | 1 | 10.9 | 19.8 |
| | 2 | 8.5 | 19.1 |
| | 3 | 7.7 | 16.8 |
| | 4 | 6.3 | 21.6 |
| | 5 | 5.8 | 18.8 |

(1) Each sample consisted of 1800 ml except 5 which was 2000 ml.

(2) Ash was determined by burning a sample of solids and measuring noncombustibles or ash. The ash derives from combined potassium acid terephthalate and potassium benzoate and of course constitutes an impurity in terephthalic acid. Feed to column 5 via pipe 6 contained 25 wt. % ash on same basis.

Samples of effluent streams from column 19, that is streams 21 and 28, were taken and analyzed with the following results set out in Tables III and IV.

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Table III (Stream 21)

| | Sample ⁽¹⁾ No. | Total Solids, ⁽²⁾ grams | Solid TPA, grams | TPA Solids, Wt. % |
|----|---------------------------|---------------------------------------|---------------------|----------------------|
| 25 | 1 | 15.9246 | 3.8279 | 24.0 |
| | 2 | 51.9828 | 8.4602 | 16.3 |
| | 3 | 29.5746 | 5.5696 | 18.8 |
| | 4 | 32.3812 | 5.0866 | 15.7 |
| | 5 | 55.4300 | 6.9924 | 12.6 |
| | 6 | 37.5153 | 4.6248 | 12.3 |
| 30 | 7 | 48.0607 | 13.6953 | 28.5 |
| | 8 | 35.6283 | 10.1130 | 28.4 |
| | 9 | 39.0367 | 14.4613 | 37.0 |
| | 10 | 32.7350 | 11.6889 | 35.7 |
| | 11 | 37.3122 | 12.1851 | 32.7 |
| | 12 | 46.1942 | 13.9704 | 30.2 |
| 35 | 13 | 8.7466 | 0.5737 | 6.56 |

(1) Each sample equaled 900 ml except 5, 7, and 2 which were 950 ml and 13 which was 350 ml. The 13 samples constituted the total overhead stream 21.

(2) Consists of both dissolved (principally potassium benzoate (KBZ) and undissolved solids (principally terephthalic acid (TPA)).

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Thus considerable impurity was removed from the terephthalic acid crystals in wash column 19 as indicated in Table III by the weight of total solids less the weight of terephthalic acid.

Table IV (Stream 28)

| | Sample No. | Sample Volume, ml | Total Solids, grams | Solids, Wt. % | Ash, Wt. % |
|----|--------------|----------------------|------------------------|---------------|------------|
| 45 | 1 | 200 | 20.8710 | 10.36 | 0.50 |
| | 2 | 200 | 25.1277 | 11.86 | 0.76 |
| | Intermediate | 900 | — | 12.05 | — |
| | 3 | 175 | 23.0127 | 13.53 | 0.74 |
| 50 | 4 | 175 | 20.6777 | 12.45 | 0.84 |

- The ash content is seen to have been reduced to only about 0.50 to 0.80 weight percent. Ash content of feed to the wash column via pipe 6 was 25 weight percent.
- 5 Hence the efficiency of the columns for removing ash or potassium containing impurities is evident.
- The slurry product in the lower portion of column 19 contained an unmeasured amount of benzoic acid which was largely removed by passing the slurry to tank 30 wherein additional wash water was added and the mixture stirred for about 15 minutes at a temperature of 193°C. The resulting slurry was 10 then passed through filter 32 and the crystal product contained in line 34 was again re-slurried in water at 193°C. The final terephthalic acid crystals recovered by a second filtration contained only about 0.02 percent 15 by weight benzoic acid and less than 10 parts per million potassium.
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- WHAT WE CLAIM IS:—**
1. A process for the preparation and recovery of terephthalic acid from an aqueous solution of dipotassium terephthalate, which comprises, in sequence,
 - (i) reacting the dipotassium terephthalate in said solution with benzoic acid to produce an aqueous slurry containing dissolved potassium benzoate and undissolved benzoic acid, potassium hydrogen terephthalate, and terephthalic acid;
 - (ii) countercurrently contacting said slurry in an elongated zone with a stream of water, the temperature in said zone adjacent the upstream end (considered in the direction of travel of the slurry) being maintained at a temperature in the range 38—66°C. and adjacent the downstream end at a lower temperature, such lower temperature being in the range 10—38°C.;
 - (iii) recovering from said upstream end an aqueous solution of potassium benzoate and from said downstream end an aqueous slurry of benzoic acid, potassium hydrogen terephthalate and terephthalic acid;
 - 45 (iv) countercurrently contacting the slurry recovered in step (iii) in a second elongated contacting zone with a second stream of water, the temperature in said second zone adjacent the upstream end (considered in the direction of travel of the slurry) being maintained at a temperature in the range 66—121°C. and adjacent the downstream end at a lower temperature, such lower temperature being in the range 24 to 66°C.;
 - (v) recovering from the upstream end of said second zone a second aqueous solution of potassium benzoate and from the downstream end an aqueous slurry of terephthalic acid; and
 - (iv) separating the terephthalic acid from the slurry recovered in step (v).
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2. A process according to claim 1, wherein, in steps ii) and iv) the respective slurries are countercurrently contacted with said water streams in vertically arranged contacting zones through which the slurries pass downwardly and the water streams pass upwardly.
3. A process according to claim 1 or 2, wherein the temperatures in the upstream and downstream ends of said first contacting zone are maintained at about 49°C. and about 27°C. respectively.
4. A process according to claim 1, 2 and 3, wherein the temperatures in the upstream and downstream ends of said second contacting zone are maintained at about 88°C. and about 38°C. respectively.
5. A process according to any one of the preceding claims, wherein the terephthalic acid recovered in step vi) is further purified by extraction with water at a temperature in the range 149 to 232°C.
6. A process according to claim 5, wherein the extraction temperature is 193°C.
7. A process according to claim 1, substantially as hereinbefore described with reference to the accompanying drawing.
8. A process according to claim 1, substantially as hereinbefore described with reference to the foregoing Example.
9. Terephthalic acid when prepared and recovered by a method according to any preceding claim.

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